FILMS WITH SUPERIOR IMPACT RESISTANCE AND IMPROVED CATASTROPHIC FAILURE RESISTANCE UNDER HIGH STRAIN RATE

The use of thermoplastic stretch wrap films for the overwrap
5   packaging of goods, and in particular, the unitizing of palleted loads is
a commercially significant application of polymer film, including
generically, polyethylene. Overwrapping a plurality of articles to provide
a unitized load can be achieved by a variety of techniques. In one
procedure, the load to be wrapped is positioned upon a platform, or
10   turntable, which is made to rotate and in so doing, to take up stretch
wrap film supplied from a continuous roll. Braking tension is applied to
the film roll so that the film is continuously subjected to a stretching,
or tensioning, force as it wraps around the rotating load in overlapping
layers. Generally, the stretch wrap film is supplied from a vertically
15   arranged roll positioned adjacent to the rotating pallet load. Rotational
speeds of from 5 to 50 revolutions per minute are common. At the
completion of the overwrap operation, the turntable is completely stopped
and the film is cut and attached to an underlying layer of film employing
tack sealing, adhesive tape, spray adhesives, etc. Depending upon the
20   width of the stretch wrap roll, the load being overwrapped can be shrouded
in the film while the vertically arranged film roll remains in a fixed
position. Alternatively, the film roll, for example, in the case of
relatively narrow film widths and relatively wide pallet loads, can be
made to move in a vertical direction as the load is being overwrapped
25   whereby a spiral wrapping effect is achieved on the packaged goods.

Another wrapping method finding acceptance in industry today is that
of hand wrapping. In this method, the film is again arranged on a roll,
however, it is hand held by the operator who walks around the goods to be
wrapped, applying the film to the goods. The roll of film so used may be
30   installed on a hand-held wrapping tool for ease of use by the operator.

Historically, higher performance stretch films have been prepared
with linear low density polyethylene made using a metallocene catalyst (m-
LLDPE), most often with the m-LLDPE located in an interior layer. Such
films have shown markedly improved puncture and impact resistance as well
35   as improved film clarity relative to counterparts made with more
traditional LLDPEs made using Ziegler-Natta catalysts. Stretch films
employing higher amounts (up to 100 wt percent) of m-LLDPE either as a
discrete layer or layers, or as a blend component in a discrete layer or
layers of a multilayer stretch film, propagate defects more easily leading
40   to web breakage. This defect propagation, also referred to as catastrophic
film failure, has precluded the development of film structures containing
higher concentrations of m-LLDPE to maximize toughness.

Accordingly, stretch films which exhibit good puncture and impact
resistance while also exhibiting resistance to defect propagation are
45   desired. The films of the present invention have an ultimate stretch of

at least about 200 percent, a dart impact strength of at least about 700 gms/mil and a catastrophic failure stretch of at least about 95 percent of the ultimate stretch value (CF of about 5 percent or less). The films preferably comprise at least 3 layers and preferably comprise at least 50
5   percent by weight of polyethylene polymers.

FIG. 1 is a diagram showing a suitable film path for a testing device for determining parameters such as ultimate stretch and catastrophic failure of films.

The films of the present invention are stretch films. Accordingly, they
10   will have an ultimate stretch of at least about 200 percent . Preferably the films will have an ultimate stretch of at least 250 percent, more preferably at least 300 percent, and can be as high as about 370 percent. Preferably, the stretch film comprises a homogeneous polymer component. More preferably, the stretch film is made at a commercial output rate, for
15   example at a rate of at least about 6 pounds/hour/inch of die width.

The ultimate stretch (or "US") is determined by the Highlight Test Stand commercially available from Highlight Industries, 2694 Prairie Street SW, Wyoming, MI 49509, in which the film starts at 0 percent stretch and is elongated until the film fails (known as the ultimate
20   stretch percent) and is displayed and graphed by the test stand. It should be understood that the ultimate stretch will be dependent upon the thickness of the film, and the stated preferences above correspond to a film having a thickness of about 0.7 mil. Figure 1 shows the film path diagram for such a testing device. In this figure, the dotted lines at the
25   film mandrel indicate that the film may feed in either direction (single-side cling film should feed such that the cling side in against the first idler roller). The solid line (A) at the take up mandrel (which rotates counterclockwise in the figure), indicates the preferred path for Ultimate, Quality, Breaks/Roll and Roller Retention tests, whereas the
30   dotted line (B) represents the preferred path for Puncture & Retention tests.

The films of the present invention may be up to 3 mils (0.0762 mm) thick, preferably in the range of 0.4 mil (0.0102 mm) to 1.0 mil (0.0254 mm)thick and even more preferred about 0.7 mil (0.0178 mm) thick.
35   The films of the present invention can be monolayer but are more preferably three or more layers. If the film is a multilayer structure, the layers may be of any desired thickness, and any desired polymeric composition. It should be understood that two or more of the layers, including adjacent layers, may be identical.
40   The films of the present invention will have relatively high dart impact strength. Dart impact strength can be determined using ASTM D1709. The films of the present invention will have a dart impact strength of at least 300 grams as measured by ASTM D1709 (Dart A) for a 0.7 mil film. More preferably the films will have a Dart A value of 400 grams or
45   greater, and most preferably 500 grams or greater for a 0.7 mil film.

While it is not believed that the relationship between dart impact strength and film thickness is linear, for thicknesses other than 0.7 mil, it is generally preferred that dart impact strength be greater than about 430 gram/mil, more preferably greater than about 570 gram/mil and most preferably greater than about 700 gram/mil.

The films of the present invention will also be resistant to catastrophic failure. Catastrophic failure can be measured using a Highlight Ultimate Stretch Tester Puncture Test, using equipment manufactured by Highlight Industries, Inc. and conducted in accord with Highlight Stretch Tester product literature and operating manuals. In this procedure, which is also referred to in the Statutory Invention Registration US H2073 H as Defect Propagation Resistance Testing, the films are stretched increasing amounts to determine the ultimate stretch percentage. At some increased percentage stretch, a defect is introduced by way of the Highlight Stretch Tester Puncture Test. As the percentage stretch is increased, at some point the film will experience a catastrophic failure initiating at the puncture point, destroying the continuity of the film. The percentage stretch at which catastrophic failure is observed is referred to herein as "CS". As above, Figure 1 shows the film path diagram for such a device.

The resistance to catastrophic failure can be characterized using the ratio of the ultimate stretch percentage minus the catastrophic failure stretch percentage divided by the ultimate stretch percentage. This ratio, hereinafter referred to as "CF" is expressed as a percentage and is defined herein to mean: 100*(US-CS)/US. Thus, for example, if the ultimate stretch for a film was 300 percent and the stretch where catastrophic failure was observed in the Highlight Stretch Puncture test was 270 percent, the CF would be 10 percent.

The films of the present invention have a CF of 5 percent or less, more preferably a CF of 4 percent or less and moist preferably a CF of 3 percent or less.

In another aspect, the invention is a stretch film having an ultimate stretch of at least 200 percent , a Dart A of at least 430 gms/mil and a CF of 5 percent or less, and comprising at least three layers, wherein a non-skin layer comprises a propylene polymer, and at least one other layer comprises an ethylene polymer composition, wherein the composition comprises:

(A) from 10 percent (by weight of the total composition) to 95 percent (by weight of the total composition) of at least one ethylene interpolymer having:

    (i) a density from 0.89 g/cm^3 to 0.935 g/cm^3,

    (ii) a melt index (I_2) from 0.001 g/10 minutes to 10 g/10 minutes,

    (iii) a slope of strain hardening coefficient greater than or equal to 1.3, and

(iv) a Composition Distribution Index (CDBI) greater than 50 percent; and

(B) from 5 percent (by weight of the total composition) to 90 percent (by weight of the total composition) of at least one ethylene polymer having a density from 0.93 g/cm^3 to 0.965 g/cm^3 and a linear polymer fraction, as determined using temperature rising elution fractionation (TREF).

In yet another aspect, the invention is a stretch film having an ultimate stretch of at least 200 percent , a Dart A of at least 430 gms/mil and a CF of 5 percent or less, and comprising at least three layers, wherein a non-skin layer comprises a propylene polymer, and at least one other layer comprises an ethylene polymer composition, wherein the composition comprises:

(A) from 10 percent (by weight of the total composition) to 100 percent (by weight of the total composition) of at least one ethylene interpolymer having:

(i) a density from 0.89 g/cm^3 to 0.935 g/cm^3,

(ii) a melt index (I$_2$)from 0.001 g/10 minutes to 10 g/10 minutes, preferably from 0.001 g/10 minutes to 1 g/10 minutes, more preferably from 0.001 g/10 minutes to 0.5 g/10 minutes,

(iii) a molecular weight distribution, Mw/Mn, from 2 to 4, and

(iv) a Composition Distribution Index (CDBI) greater than 50 percent; and

(B) optionally, from 5 percent or less (by weight of the total composition) to 90 percent (by weight of the total composition) of at least one ethylene polymer having a density from 0.93 g/cm^3 to 0.965 g/cm^3 and a linear polymer fraction, as determined using temperature rising elution fractionation (TREF).

In still another aspect, the invention is a stretch film having an ultimate stretch of at least 200 percent , a Dart A of at least 430 gms/mil and a CF of 5 percent or less, and comprising at least three layers, wherein a non-skin layer comprises a propylene polymer, and at least one other layer comprises an ethylene polymer composition, wherein the composition comprises:

(A) an ethylene interpolymer having a molecular weight distribution, M$_w$/M$_n$, of less than about 3, and a narrow composition distribution breadth index (CDBI), defined as the weight percent of the polymer molecules having a comonomer content within 50 percent of the median total molar comonomer content, which is greater than about 50 percent and a degree of branching less than or equal to 2 methyls/1000 carbons of about 15 percent (by weight) or less, said interpolymer A being present in an amount of from 15 to 85 percent by weight based on the combined weight of Components A and B; and

(B) an interpolymer having a molecular weight distribution, M_w/M_n, of 3 or more and a broad composition distribution and a degree of branching less than or equal to 2 methyls/1000 carbons of about 10 percent (by weight) or more and a degree of branching greater than or equal to 25
5   methyls/1000 carbons of from about 25 percent (by weight) or less present in the interpolymer composition, said interpolymer B being present in an amount of from 15 to 85 percent by weight based on the combined weight of Components A and B.
Preferably, the ethylene compositions described in the last three
10 embodiments comprise a skin layer.

The films can be made from any polymer capable of achieving the stretch films having the indicated impact resistance and resistance to catastrophic failure. It is generally preferred that the film be
15 comprised of polyethylene homopolymers or copolymers, and preferably such polymers make up at least about 50 percent by weight of the film. Polyethylene homopolymers include all types of homopolymers, including gas phase, slurry and solution produced homopolymers. Polyethylene copolymers include ethylene/C_3-C_{20} alpha-olefins, especially ethylene/1-hexene
20 copolymers, ethylene/4-methyl-1-pentene copolymers, and ethylene/1-octene copolymers. Types of polyethylene, both copolymers and homopolymers, can advantageously be selected for the desired combination of other properties, such as clarity and cling. These types of polyethylene include metallocene polyethylene, such as that described in USP 5,278,272
25 and USP 5,272,236, as well as Ziegler-Nata polyethylene, such as that described in USP 4,076,698, the disclosures of all of which are incorporated herein by reference. Of course, one skilled in the art of film manufacture knows that the molecular·weight is chosen for optimum film performance, as well as physical properties desired. Similarly,
30 polymer density is also selected for performance, including desired film stiffness. Various film manufacturing techniques can be used, such as blown, cast and extrusion coated, although cast film is preferred. In-situ reactor "blends" are also useful in the film structures of the invention. The polymer materials can be described as in USP 5,844,045 and USP
35 6,111,023, the disclosures of which are incorporated herein by reference.
Such film structures may be made by conventional fabrication techniques, *for example* simple bubble extrusion, biaxial orientation processes (such as tenter frames or double bubble processes), simple cast/sheet extrusion, coextrusion, lamination, *etc.* Conventional simple
40 bubble extrusion processes (also known as hot blown film processes) are described, for example, in The Encyclopedia of Chemical Technology, Kirk-Othmer, Third Edition, John Wiley & Sons, New York, 1981, Vol. 16, pp. 416-417 and Vol. 18, pp. 191-192, the disclosures of which are incorporated herein by reference. Biaxial orientation film manufacturing

processes such as described in the "double bubble" process of
U.S.-A-Patent No. 3,456,044 (Pahlke), and the processes described in
U.S.-A-Patent No. 4,352,849 (Mueller), U.S.-A-Patent Nos. 4,820,557 and
4,837,084 (both to Warren), U.S.-A-Patent No. 4,865,902 (Golike *et al.*),
5 U.S.-A-Patent No. 4,927,708 (Herran *et al.*), U.S.-A-Patent No. 4.952,451
(Mueller), and U.S.-A-Patent Nos. 4,963,419 and 5,059,481 (both to Lustig
et al.), the disclosures of which are incorporated herein by reference,
can also be used to make the novel film structures of this invention.

Polymers other than polyethylenes can also be advantageously used in
10 the present invention. Propylene polymers include polypropylene
homopolymer and copolymers, including random and impact copolymers, such
as propylene/ethylene copolymers and are particularly well suited for use
in the present invention. Propylene polymers having a 2 percent secant
modulus, as measured by ASTM D 882, of about 150,000 psi and less are
15 preferred. Propylene polymers include those commercially available from
ExxonMobil (VISTAMAXX™) and The Dow Chemical Company (for example,
INSPIRE™ and VERSIFY™). In certain applications it may also be desirable
to have one or more layers of the film structure comprise a styrenic block
copolymer (such as SBS, SEBS, SIS, SIBS etc.), EPDM rubber or EPR, or
20 multi-block copolymers such as thermoplastic elastomers based on
polyurethanes, polyethers and polyamides. In the propylene polymers
useful in this invention, the polymers comprise at least 50 percent (by
weight) propylene monomer units.

Stretch film comprising the compositions disclosed herein are also
25 within the scope of the invention, wherein at least one non-surface layer
(also known as a non-skin layer) comprises at least one propylene polymer.

In another aspect, the invention is a stretch film comprising at
least one layer comprising an ethylene polymer, wherein the film has a
tensile stress at break of at least 5000 psi and an ultimate stretch of at
30 least 200 percent , a Dart A of at least 430 gms/mil and a CF of 5 percent
or less. Preferably, the film contains a non-surface layer comprising at
least one propylene polymer.

In still another aspect, the invention is a stretch film comprising
at least one layer comprising an ethylene polymer, wherein the film has a
35 tensile stress at break of at least 5000 psi and an ultimate stretch of at
least 200 percent and a CF of 5 percent or less. Preferably, the film
contains a non-surface layer comprising at least one propylene polymer.

In multilayer films it was observed that the choice of compositions
used for internal layers appeared to effect the CF values more than the
40 polymer composition for the outside layers. Thus it is preferred that one
or more of the core (or non-surface) layers of the film comprise a
heterogeneously branched polyethylene characterized as having: a density
from 0.9 g/cc to 0.96 g/cc; a melt index from 0.5 g/10 minutes to 10 g/10

minutes, measured in accordance with ASTM D 1238, condition 190C/2.16 kg;
and a molecular weight distribution from 2.5 to 4.5.

EXAMPLES

All cast film samples are fabricated on a 5-layer Egan cast film
line consisting of three 2.5 in. and two 2.0 in. 30:1 L/D Egan Model MAC
6530 air cooled extruders. A Chloren 5-layer adjustable vane feedblock
and 36 in. EPOCH III autogauge 5.1 coat hanger die with a .020 in. die gap
are utilized during this evaluation. Extruder barrel temperatures are
adjusted based on the resin and pumping rates to maintain a constant melt
temperature. The die zone temperatures correspond to the polymer melt
temperature, approx. 525 degrees F. Line speeds are controlled at 700 fpm
by the CMR 2000 microprocessor while film thickness (.7 mil) is measured
utilizing a NDC thickness gauge. Both primary and secondary chill roll
temperatures are held at a constant 70 degrees F. Air gap is maintained
at approximately 3.5" for all samples. An air knife is used to pin the
film to the chill roll.

Ultimate tensile strain percentage and ultimate tensile stress are
tested as described in ASTM D882. Ultimate stretch and catastrophic
failure percentages are obtained utilizing a Highlight test stand
manufactured by Highlight Industries, Inc. Dart A impact resistance is
measured as described in ASTM D1709 and is tested on unstretched film.

In the following Examples, Resin A is an ethylene/1-octene
copolymer, comprising about 51 percent (by weight) of a metallocene
component having a melt index of about 1.85 g/10 minutes and a density of
about 0.910 g/cc and about 49 percent of a Ziegler Natta component having
a melt index of about 5.04 g/10 minutes and a density of about 0.923 g/cc;
the final polymer composition has a melt index of about 4.0 g/10 minutes
and a density of about 0.916 g/cc. Such polymers can be made according to
USP 5,844,045, USP 5,869,575, USP 6,448,341, the disclosures of which are
incorporated herein by reference. Melt index is measured in accordance
with ASTM D-1238, condition 190 C/2.16 kg and density is measured in
accordance with ASTM D-792.

Resin B is an ethylene polymer having a density of 0.918 g/cc and a
melt index (190°C) of 3.5 g/10 minutes (ASTM D1238), commercially
available from the ExxonMobil Company as Exceed™ 3518.

Resin C is homopolymer polypropylene produced via the Unipol process
from The Dow Chemical Company, having a density of 0.90 g/cc and a melt
flow rate (230 °C) of 8.7 g/10 min. (ASTM D1238).

Resin D is a blend comprising 85 percent by weight of Resin C and 15
percent of an ethylene plastomer produced via INSITE* Technology from Dow,
having a density of 0.87 g/cc and a melt index (190 °C) of 5.0 g/10 min.
(ASTM D1238). This resin is commercially available from The Dow Chemical
Company as AFFINITY™ EG8200.

Resin E is linear low density polyethylene produced by the solution
process, having a density of 0.941 g/cc and a melt index (190 °C) of 4.0

g/10 min. (ASTM D1238). This resin is commercially available from The Dow
Chemical Company as DOWLEX™ 2027G.

    For comparative examples 1 and 3 and Examples 1 and 2, a series of
films consisting of Resin A/Resin A/Core layer/Resin A /Resin A with a
5   layer ratio of 10/35/10/35/10 were fabricated. In comparative Example 2,
the film consisted of Resin B in all 5 layers. In comparative Example 4,
the film consisted of Resin E/Resin A/Resin A/Resin A/Resin A with a layer
ratio of 10/35/10/35/10. The performance properties of the films are
compared in Table I below.

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Table I

	Comp.1	Comp 2	Comp. 3	Example 1	Example 2	Comp 4
Core Layer Composition	Resin A	Resin B	Resin C	Resin D	Resin E	Resin A
Gauge- (mils)	0.7	0.7	0.8	0.7	0.7	0.7
US (percent)	317	311	378	327	342	339
CS (percent)	290	255	370	325	341	295
CF (percent)	9	18	3	1	0	13
Dart A (grams)	850	820	208	668	306	178

    Comparative 1 and Comparative 2 showed undesirably low catastrophic
15   failure strain values (CS) of <305 percent, and undesirably high
catastrophic failure values (CF) (>10 percent). Comparative 3 showed
undesirably low impact resistance (<300 grams). The Example 1 of this
invention showed high catastrophic failure strain (364 percent) and good
dart impact strength (668 grams). Example 2 of this invention showed high
20   catastrophic failure strain (341 percent) and acceptable dart impact
strength (306 grams).